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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the new electrolysis solution for lithium secondary batteries which can provide the lithium secondary battery excellent also in battery characteristics, such as the cycle characteristic of a cell, electric capacity, a conservation characteristic, and the lithium secondary battery using it.

[0002]

[Description of the Prior Art]In recent years, the lithium secondary battery is widely used as power supplies for a drive, such as sized electronic equipment. The lithium secondary battery mainly comprises an anode, nonaqueous electrolyte, and a negative electrode.

In particular, lithium multiple oxides, such as LiCoO_2 , are used as an anode, and the lithium secondary battery which used the carbon material or the lithium metal as the negative electrode is used suitably. And as a nonaqueous solvent of the electrolysis solution for lithium secondary batteries, Carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and methylethyl carbonate (MEC), is used suitably.

[0003]

[Problem(s) to be Solved by the Invention]However, the rechargeable battery which has the further outstanding characteristic about battery characteristics, such as the cycle characteristic of a cell and electric capacity, is called for. The solvent in nonaqueous electrolyte carries out oxidative degradation of the lithium secondary battery, for example, using LiCoO_2 , LiMn_2O_4 , LiNiO_2 , etc. as positive active material in part locally at the time of charge, and in order that this decomposition product may check the desirable electrochemical reaction of a cell, it produces the fall of battery capacity. This is considered to originate in the electrochemical oxidation of the solvent in the interface of a positive electrode material and nonaqueous electrolyte. As negative electrode active material, exfoliation of carbon negative electrode material is observed and the lithium secondary battery using high-crystallized carbon materials, such as natural graphite and an artificial graphite, may become irreversible [capacity] according to the grade of a phenomenon. This exfoliation takes place, when the solvent in an electrolysis solution decomposes at the time of charge, and it originates in the electrochemical reduction of the solvent in the interface of carbon negative electrode material and an electrolysis solution. Especially, although the electrolysis solution using

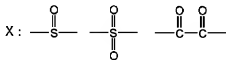
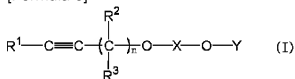
PC with the low melting point and a high dielectric constant had high electrical conduction also in low temperature, when a graphite negative electrode was used, disassembly of PC took place, and lithium secondary batteries had the problem that it could not be used. While EC also repeats charge and discharge, a solution happens in part, and the fall of battery capacity takes place. For this reason, the actual condition is that battery characteristics, such as the cycle characteristic of a cell and electric capacity, are not necessarily satisfactory.

[0004] This invention solves SUBJECT about the above electrolysis solutions for lithium secondary batteries. It aims at providing the electrolysis solution for lithium secondary batteries which can constitute the lithium secondary battery which was excellent in the cycle characteristic of a cell and was further excellent also in battery characteristics, such as electric capacity and a conservation characteristic in a charging state, and the lithium secondary battery using it.

[0005]

[Means for Solving the Problem] In an electrolysis solution by which an electrolyte is dissolved in a nonaqueous solvent, this invention is following general formula (I) in this electrolysis solution, [0006]

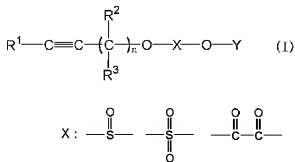
[Formula 3]



[0007] (R^1 , R^2 , and R^3 show the alkyl group of the carbon numbers 1-12, the cycloalkyl group of the carbon numbers 3-6, the aryl group of the carbon numbers 6-12, the aralkyl group of the carbon numbers 7-12, or a hydrogen atom independently among a formula, respectively.) It may combine with each other and R^2 and R^3 may form the cycloalkyl group of the carbon numbers 3-6. However, n shows the integer of 1 or 2. X are shown among a formula and a sulfoxide group, a sulfone group, and an OGIZARIRU group Y . The alkyl group of the carbon numbers 1-12, an alkenyl group, an alkynyl group, the cycloalkyl group of the carbon numbers 3-6, The aryl group of the carbon numbers 6-12 or the aralkyl group of the carbon numbers 7-12 is shown. It is related with the electrolysis solution for lithium secondary batteries, wherein at least one sort in the alkyne derivative expressed contains.

[0008] This invention is following general formula (I) in this electrolysis solution in a lithium secondary battery which consists of an electrolysis solution by which an electrolyte is dissolved in an anode, a negative electrode, and a nonaqueous solvent, [0009]

[Formula 4]



[0010] (R^1 , R^2 , and R^3 show the alkyl group of the carbon numbers 1-12, the cycloalkyl group of the carbon numbers 3-6, the aryl group of the carbon numbers 6-12, the aralkyl group of the carbon numbers 7-12, or a hydrogen atom independently among a formula, respectively.) It may combine with each other and R^2 and R^3 may form the cycloalkyl group of the carbon numbers 3-6. However, n shows the integer of 1 or 2. X are shown among a formula and a sulfoxide group, a sulfone group, and an OGIZARIRU group Y . The alkyl group of the carbon numbers 1-12, an alkenyl group, an alkynyl group, the cycloalkyl group of the carbon numbers 3-6, The aryl group of the carbon numbers 6-12 or the aralkyl group of the carbon numbers 7-12 is shown. It is related with a lithium secondary battery, wherein at least one sort in the alkyne derivative expressed contains.

[0011] Said alkyne derivative contained in an electrolysis solution, It is presumed that these some decomposition products prevent reduction disassembly of an organic solvent in an electrolysis solution by forming passive film in the high-crystallized activity carbon negative electrode surfaces, such as natural graphite and an artificial graphite, by carrying out reduction decomposition ahead of an organic solvent in an electrolysis solution on the carbon negative electrode surface at the time of charge. It is presumed that potential on the surface of a positive electrode material carries out oxidative degradation of these some decomposition products ahead of an organic solvent in an electrolysis solution in a very small excess voltage portion which became high too much, and it prevents oxidative degradation of an organic solvent in an electrolysis solution. It is thought that it has an effect which controls disassembly of an electrolysis solution without this spoiling a normal reaction of a cell.

[0012]

[Embodiment of the Invention] In the alkyne derivative expressed with said general formula (I) contained in the electrolysis solution by which the electrolyte is dissolved in the nonaqueous solvent, R^1 , R^2 , and R^3 , The alkyl group of the carbon numbers 1-12 independently like a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group respectively is preferred. A branching alkyl group like an isopropyl group and an isobutyl group may be sufficient as an alkyl group. The cycloalkyl group of the carbon numbers 3-6 like a cyclopropyl group and a cyclohexyl group may be sufficient. The aralkyl group of the carbon numbers 7-12 like a phenyl group, the aryl group of the carbon numbers 6-12 like p-tolyl group or benzyl, and a phenethyl group may be contained. R^2 and R^3 may form the cycloalkyl group of the carbon numbers 3-6 like the cyclopropyl group which was combined mutually and combined with 2-5 ethylene chains, a cyclobutyl group, a cyclopentyl group, and a cyclohexyl group. However, n shows the integer of 1 or 2.

[0013] X in the alkyne derivative expressed with said general formula (I) has a sulfoxide group, a sulfone

group, and a preferred OGIZARIRU group. The alkyl group of Y of the carbon numbers 1-12 like a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, and a hexyl group is preferred. A branching alkyl group like an isopropyl group and an isobutyl group may be sufficient as an alkyl group. The cycloalkyl group of the carbon numbers 3-6 like a cyclopropyl group and a cyclohexyl group may be sufficient. The aralkyl group of the carbon numbers 7-12 like a phenyl group, the aryl group of the carbon numbers 6-12 like p-tolyl group or benzyl, and a phenethyl group may be contained. Y A methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, It may be an alkynyl group of the carbon numbers 3-12 like the alkyl group of the carbon numbers 1-12 like a hexyl group, a vinyl group, the alkenyl group of the carbon numbers 2-12 like an allyl group, 2-propynyl group, or 3-butynyl group and 1-methyl-2-propynyl group. Y may be an alkynyl group which has R^1 which becomes a symmetrical compound focusing on X in general formula (I), R^2 , and R^3 .

[0014]As an example of an alkyne derivative expressed with said general formula (I), when X is a sulfoxide group, it is a JI (2-propynyl) ape fight, for example. [An $R^1=R^2=R^3$ = hydrogen atom, Y= 2-propynyl group, n= 1] JI (1-methyl-2-propynyl) ape fight [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y=1-methyl-2-propynyl group, n= 1] JI (2-butynyl) ape fight [An R^1 = methyl group and $R^2=R^3$ = hydrogen atom, a Y=2-butynyl group, n= 1] JI (3-butynyl) ape fight [An $R^1=R^2=R^3$ = hydrogen atom, a Y=3-butynyl group, n= 2] JI (2-pentynyl) ape fight [An R^1 = ethyl group and $R^2=R^3$ = hydrogen atom, a Y=2-pentynyl group, n= 1] JI (1-methyl-2-butynyl) ape fight [An $R^1=R^2$ = methyl group, an R^3 = hydrogen atom, a Y=1-methyl-2-butynyl group, n= 1] JI (1,1-dimethyl- 2-propynyl) ape fight [An R^1 = hydrogen atom and $R^2=R^3$ = methyl group, Y=1,1-dimethyl- 2-propynyl group, n= 1] JI (1,1-diethyl- 2-propynyl) ape fight [An R^1 = hydrogen atom and $R^2=R^3$ = ethyl group, Y=1,1-diethyl- 2-propynyl group, n= 1] JI (1-ethyl-1-methyl-2-propynyl) ape fight [An R^1 = hydrogen atom, an R^2 = ethyl group, an R^3 = methyl group, Y=1-ethyl-1-methyl-2-propynyl group, n= 1] JI (1-isobutyl-1-methyl-2-propynyl) ape fight [An R^1 = hydrogen atom, an R^2 = isobutyl group, an R^3 = methyl group, a Y=1-isobutyl-1-methyl-propynyl group, n= 1] JI (1,1-dimethyl- 2-butynyl) ape fight [An $R^1=R^2=R^3$ = methyl group, a Y=1,1-dimethyl- 2-butynyl group, n= 1] JI (1-ethynylcyclohexyl) ape fight A [R^1 = hydrogen atom, R^2 , and R^3 are a combination = pentamethylene group, a Y=1-ethynyl cyclohexyl group, and n=1]. JI (1-methyl-1-phenyl-2-propynyl) ape fight [An R^1 = hydrogen atom, an R^2 = phenyl group, an R^3 = methyl group, Y=1-methyl-1-phenyl-2-propynyl group, n= 1] JI (1,1-diphenyl-2-propynyl) ape fight [An R^1 = hydrogen atom and $R^2=R^3$ = phenyl group, Y=1,1-diphenyl-2-propynyl group, n= 1] Methyl 2-propynyl ape fight [An $R^1=R^2=R^3$ = hydrogen atom, Y= methyl group, n= 1] Methyl 1-methyl-2-propynyl ape fight [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y= methyl group, n= 1] Ethyl 2-propynyl ape fight [An $R^1=R^2=R^3$ = hydrogen atom, Y= ethyl group, n= 1] Phenyl 2-propynyl ape fight [An $R^1=R^2=R^3$ = hydrogen atom, Y= phenyl group, n= 1] Cyclohexyl 2-propynyl ape fight [An $R^1=R^2=R^3$ = hydrogen atom, Y= cyclohexyl group, n= 1] **** is mentioned. However, this invention is not limited to these compounds at all.

[0015]As an example of an alkyne derivative expressed with said general formula (I), when X is a sulfone group, it is JI (2-propynyl) sulfate, for example. [An $R^1=R^2=R^3$ = hydrogen atom, Y= 2-propynyl group, n= 1] JI (1-methyl-2-propynyl) sulfate [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y=1-methyl-2-propynyl group, n= 1] JI (2-butynyl) sulfate [An R^1 = methyl group and $R^2=R^3$ = hydrogen atom, a Y=2-butynyl group, n= 1] JI (3-butynyl) sulfate [An $R^1=R^2=R^3$ = hydrogen atom, a Y=3-butynyl group, n= 2] JI (2-pentynyl) sulfate [An R^1 = ethyl group and $R^2=R^3$ = hydrogen atom, a Y=2-pentynyl group, n= 1] JI (1-methyl-2-butynyl) sulfate [An $R^1=R^2$ = methyl group, an R^3 = hydrogen atom, a Y=1-methyl-2-butynyl group, n= 1] JI (1,1-dimethyl- 2-propynyl) sulfate [An R^1 = hydrogen atom and $R^2=R^3$ = methyl group, Y=1,1-dimethyl- 2-propynyl group, n= 1] JI (1,1-diethyl- 2-propynyl) sulfate [An R^1 = hydrogen atom and $R^2=R^3$ = ethyl group, Y=1,1-diethyl- 2-propynyl group, n= 1] JI (1-ethyl-1-methyl-2-propynyl) sulfate [An R^1 = hydrogen atom, an R^2 = ethyl group, an R^3 = methyl group, Y=1-ethyl-1-methyl-2-propynyl group, n= 1] JI (1-isobutyl-1-methyl-2-propynyl) sulfate [An R^1 = hydrogen atom, an R^2 = isobutyl group, an R^3 = methyl group, Y=1-isobutyl-1-methyl-2-propynyl group, n= 1] JI (1,1-dimethyl- 2-butynyl) sulfate [An $R^1=R^2=R^3$ = methyl group, a Y=1,1-dimethyl- 2-butynyl group, n= 1] JI (1-ethynylcyclohexyl) sulfate A [R^1 = hydrogen atom, R^2 , and R^3 are a combination = pentamethylene group, a Y=1-ethynyl cyclohexyl group, and n=1]. JI (1-methyl-1-phenyl-2-propynyl) sulfate [An R^1 = hydrogen atom, an R^2 = phenyl group, an R^3 = methyl group, Y=1-methyl-1-phenyl-2-propynyl group, n= 1] JI (1,1-diphenyl-2-propynyl) sulfate [An R^1 = hydrogen atom and $R^2=R^3$ = phenyl group, Y=1,1-diphenyl-2-propynyl group, n= 1] Methyl 2-propynyl sulfate [An $R^1=R^2=R^3$ = hydrogen atom, Y= methyl group, n= 1] Methyl 1-methyl-2-propynyl sulfate [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y= methyl group, n= 1] Ethyl 2-propynyl sulfate [An $R^1=R^2=R^3$ = hydrogen atom, Y= ethyl group, n= 1] Phenyl 2-propynyl sulfate [An $R^1=R^2=R^3$ = hydrogen atom, Y= phenyl group, n= 1] Cyclohexyl 2-propynyl sulfate [An $R^1=R^2=R^3$ = hydrogen atom, Y= cyclohexyl group, n= 1] **** is mentioned. However, this invention is not limited to these compounds at all.

[0016]As an example of an alkyne derivative expressed with said general formula (I), when X is an OGIZARIRU group, it is a JI (2-propynyl) OGIZA rate, for example. [An $R^1=R^2=R^3$ = hydrogen atom, Y= 2-propynyl group, n= 1] JI (1-methyl-2-propynyl) OGIZA rate [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y=1-methyl-2-propynyl group, n= 1] JI (2-butynyl) OGIZA rate [An R^1 = methyl group and $R^2=R^3$ = hydrogen atom, a Y=2-butynyl group, n= 1] JI (3-butynyl) OGIZA rate [An $R^1=R^2=R^3$ = hydrogen atom, a Y=3-butynyl group, n= 2] JI (2-pentynyl) OGIZA rate [An R^1 = ethyl group and $R^2=R^3$ = hydrogen atom, a Y=2-pentynyl group, n= 1] JI (1-methyl-2-butynyl) OGIZA rate [An $R^1=R^2$ = methyl group, an R^3 = hydrogen atom, a Y=1-methyl-2-butynyl group, n= 1] JI (1,1-dimethyl- 2-propynyl) OGIZA rate [An R^1 = hydrogen atom and $R^2=R^3$ = methyl group, Y=1,1-dimethyl- 2-propynyl group, n= 1] JI (1,1-diethyl- 2-propynyl) OGIZA rate [An R^1 = hydrogen atom and $R^2=R^3$ = ethyl group, Y=1,1-diethyl- 2-propynyl group, n= 1] JI (1-ethyl-1-methyl-2-propynyl) OGIZA rate [An R^1 = hydrogen atom, an R^2 = ethyl group, an R^3 = methyl

group, $Y=1$ -ethyl-1-methyl-2-propynyl group, $n=1$] JI (1-isobutyl-1-methyl-2-propynyl) OGIZA rate [An R^1 = hydrogen atom, an R^2 = isobutyl group, an R^3 = methyl group, $Y=1$ -isobutyl-1-methyl-2-propynyl group, $n=1$] JI (1,1-dimethyl- 2-butynyl) OGIZA rate [An $R^1=R^2=R^3$ = methyl group, a $Y=1,1$ -dimethyl- 2-butynyl group, $n=1$] JI (1-ethynylcyclohexyl) OGIZA rate A [R^1 = hydrogen atom, R^2 , and R^3 are a combination = pentamethylene group, a $Y=1$ -ethynyl cyclohexyl group, and $n=1$]. JI (1-methyl-1-phenyl-2-propynyl) OGIZA rate [An R^1 = hydrogen atom, an R^2 = phenyl group, an R^3 = methyl group, $Y=1$ -methyl-1-phenyl-2-propynyl group, $n=1$] JI (1,1-diphenyl-2-propynyl) OGIZA rate [An R^1 = hydrogen atom and $R^2=R^3$ = phenyl group, $Y=1,1$ -diphenyl-2-propynyl group, $n=1$] Methyl 2-propynyl OGIZA rate [An $R^1=R^2=R^3$ = hydrogen atom, Y = methyl group, $n=1$] Methyl 1-methyl-2-propynyl OGIZA rate [An R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Y = methyl group, $n=1$] Ethyl 2-propynyl OGIZA rate [An $R^1=R^2=R^3$ = hydrogen atom, Y = ethyl group, $n=1$] Phenyl 2-propynyl OGIZA rate [An $R^1=R^2=R^3$ = hydrogen atom, Y = phenyl group, $n=1$] Cyclohexyl 2-propynyl OGIZA rate [An $R^1=R^2=R^3$ = hydrogen atom, Y = cyclohexyl group, $n=1$] **** is mentioned. However, this invention is not limited to these compounds at all.

[0017]In said alkyne derivative, the content of an alkyne derivative expressed with said general formula (I), Since the battery characteristic which sufficient coat was not formed but was expected will not be obtained if too small [when too large, the electric conductivity of an electrolysis solution, etc. may change and battery capacity may fall, and], 0.1 to 10% of the weight of the range is especially preferred 0.01 to 20% of the weight to the weight of an electrolysis solution.

[0018]As a nonaqueous solvent used by this invention, for example Ethylene carbonate (EC), Propylene carbonate (PC), butylene carbonate (BC), Cyclic carbonate, such as vinylene carbonate (VC), and lactone, such as gamma-butyrolactone. Dimethyl carbonate (DMC), methylethyl carbonate (MEC), Chain carbonate, such as diethyl carbonate (DEC), a tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1, 2-dimethoxyethane, Amide, such as ester species, such as nitril, such as ether, such as 1,2-diethoxyethane and 1,2-dibutoxyethane, and acetonitrile, methyl propionate, methyl pivalate, and octyl pivalate, and dimethylformamide, is mentioned.

[0019]These nonaqueous solvents may be used by one kind, and may be used combining two or more kinds. Although the combination in particular of a nonaqueous solvent is not limited, various combination, such as combination of cyclic carbonate and chain carbonate, combination of cyclic carbonate and lactone, and combination of three kinds of cyclic carbonate and chain carbonate, is mentioned, for example.

[0020]As an electrolyte used by this invention, for example $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiC(SO_2CF_3)_3$, $LiPF_4(CF_3)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, $LiPF_3(iso-C_3F_7)_3$, $LiPF_5(iso-C_3F_7)$, etc. are mentioned. These electrolytes may be used by one kind, and they may be used, combining them two or more kinds. 0.1-3 M of these electrolytes are usually preferably dissolved and used for the aforementioned nonaqueous solvent by the concentration of 0.5-1.5M.

[0021]The nonaqueous electrolyte of this invention is obtained by mixing the aforementioned nonaqueous solvent, dissolving the aforementioned electrolyte in this for example, and dissolving at least one sort in the alkyne derivative expressed with said formula (I).

[0022]The nonaqueous electrolyte of this invention is suitably used as the members forming of a rechargeable battery, especially members forming of a lithium secondary battery. Especially about members forming other than the nonaqueous electrolyte which constitutes a rechargeable battery, it is not limited but various members forming currently used conventionally can be used.

[0023]For example, the composite metal oxide of at least one kind of metal and lithium which are chosen from the group which consists of cobalt, manganese, nickel, chromium, iron, and vanadium as positive active material is used. As such a composite metal oxide, LiCoO_2 , LiMn_2O_4 , LiNiO_2 , and $\text{LiCo}_{1-x}\text{nickel}_x\text{O}_2$ ($0.01 < x < 1$) etc. are mentioned, for example. It may be used like LiCoO_2 , LiMn_2O_4 and LiCoO_2 , LiNiO_2 and LiMn_2O_4 , and LiNiO_2 , mixing suitably.

[0024]An anode the aforementioned positive active material Conducting agents, such as acetylene black and carbon black, Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), The copolymer (SBR) of styrene and butadiene, the copolymer (NBR) of acrylonitrile and butadiene, After kneading with binders, such as carboxymethyl cellulose (CMC), and a solvent and considering it as positive electrode mixture, this positive electrode material is applied to the Russ board of the aluminium foil as a charge collector, or the product made from stainless steel, It is produced after desiccation and application-of-pressure molding by heat-treating under a vacuum at the temperature of 50 ° - about 250 ° for about 2 hours.

[0025]The carbon material as negative electrode active material which can emit [occlusion and] a lithium metal, a lithium alloy, or lithium [Pyrolytic carbon, corks, graphite, an organic polymer compound (artificial-graphite, natural graphite, etc.) combustion body, carbon fiber] Or substances, such as a compound tin oxidation thing, are used. It is preferred that the spacing (d_{002}) of a lattice plane (002) uses especially the carbon material which has a graphite mold crystal structure which is 0.335-0.340 nm (nano meter). Powder material like a carbon material An ethylene propylene diene terpolymer (EPDM), Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), It kneads with binders, such as a copolymer (SBR) of styrene and butadiene, a copolymer (NBR) of acrylonitrile and butadiene, and carboxymethyl cellulose (CMC), and is used as negative electrode mixture.

[0026]The structure in particular of a lithium secondary battery is not limited, and a cylindrical cell, a square-shaped cell, etc. which have the anode of a monolayer or a double layer, a negative electrode, the coin type cell which has a separator and a polymer battery, an anode of further rolled form, a negative electrode, and a rolled form separator are mentioned as an example. The fine porous membrane of polyolefine publicly known as a separator, textile fabrics, a nonwoven fabric, etc. are used.

[0027]

[Example]Next, an example and a comparative example are given and this invention is explained concretely.

Example 1 [Preparation of an electrolysis solution] After preparing the nonaqueous solvent of PC/DMC (capacity factor) =3/7, dissolving so that it may become the concentration of 1M about LiPF_6 at this, and preparing an electrolysis solution, it is a JI (2-propynyl) ape fight as an alkyne derivative further. [The inside of general formula (I), an $\text{R}^1=\text{R}^2=\text{R}^3=$ hydrogen atom and $\text{X}=\text{sulfoxide group}$, $\text{Y}=\text{2-propynyl group}$, and $n=1$] were added so that it might become 0.5 % of the weight to an electrolysis solution.

[0028][Production of a lithium secondary battery, and measurement of a battery characteristic] Acetylene

black (conducting agent) was mixed 10% of the weight 80% of the weight, polyvinylidene fluoride (binder) was mixed for LiCoO_2 (positive active material) at 10% of the weight of a rate, the 1-methyl-2-pyrrolidone was added to this, and it was made slurry form, and applied on aluminum foil. Then, pressing of this was dried and carried out and the anode was prepared. The artificial graphite (negative electrode active material) was mixed 90% of the weight, polyvinylidene fluoride (binder) was mixed at 10% of the weight of a rate, the 1-methyl-2-pyrrolidone was added to this, and it was made slurry form, and applied on copper foil. Then, pressing of this was dried and carried out and the negative electrode was prepared. And using the separator of a polypropylene fine porous film, the above-mentioned electrolysis solution was poured in and the coin cell (20 mm in diameter and 3.2 mm in thickness) was produced. After charging to 4.2V by 0.8 mA of constant current under a room temperature (20 °C) using this coin cell, it charged under the constant voltage as the final voltage 4.2V for a total of 5 hours. Next, it discharged to the final voltage 2.7V under 0.8 mA of constant current, and this charge and discharge were repeated. Initial service capacity was computed as the relative capacitor as compared with the case (comparative example 2) where $1\text{M LiPF}_6 + \text{PC/EC/DEC}$ (capacity factor) = 5/25/70 are used as an electrolysis solution, and was 0.98. When the battery characteristic after 50 cycles was measured, and initial service capacity was made into 100%, the service capacity maintenance factor was 90.1%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0029]Used the example 2 JI (2-propynyl) alkyne 2% of the weight to the electrolysis solution, and also a coin cell is produced like Example 1, When the battery characteristic was measured, the relative capacitor of initial service capacity was 0.97, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 90.7%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0030]Used the example 3 JI (2-propynyl) alkyne 5% of the weight to the electrolysis solution, and also a coin cell is produced like Example 1, When the battery characteristic was measured, the relative capacitor of initial service capacity was 0.96, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 90.5%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0031]It is methyl 2-propynyl sulfate as example 4 alkyne derivative. [The inside of general formula (I), an $\text{R}^1 = \text{R}^2 = \text{R}^3 =$ hydrogen atom, $\text{Y} =$ methyl group, When $n = 1$] was used 2% of the weight to the electrolysis solution, and also the coin cell was produced like Example 1 and the battery characteristic was measured, the relative capacitor of initial service capacity was 0.97, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 89.8%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0032]It is a JI (2-propynyl) OGIZA rate as example 5 alkyne derivative. [The inside of general formula (I), an $\text{R}^1 = \text{R}^2 = \text{R}^3 =$ hydrogen atom, $\text{X} =$ OGIZARIRU group, When $\text{Y} =$ 2-propynyl group and $n = 1$] were used 2% of the weight to the electrolysis solution, and also the coin cell was produced like Example 1 and the battery characteristic was measured, the relative capacitor of initial service capacity was 0.97, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 90.2%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0033]The nonaqueous solvent of comparative example 1 PC/DMC(capacity factor) =3/7 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF_6 at this. At this time, the alkyne derivative was not added at all. When the coin cell was produced like Example 1 using this electrolysis solution and the battery characteristic was measured, it turned out that charge and discharge are not carried out. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0034]After preparing the nonaqueous solvent of example 6 PC/EC/DEC(capacity factor) =5/25/70, dissolving so that it may become the concentration of 1M about LiPF_6 at this, and preparing an electrolysis solution, it is a JI (1-methyl-2-propynyl) ape fight as an alkyne derivative further. [The inside of general formula (I), an R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, X= sulfoxide group, Y=1-methyl-2-propynyl group, and n= 1] were added so that it might become 2 % of the weight to an electrolysis solution. When a coin cell is produced like Example 1 using this electrolysis solution and a battery characteristic is measured, initial service capacity, As compared with the case (comparative example 2) where 1M LiPF_6 +PC/EC/DEC(capacity factor) =5/25/70 are used as an electrolysis solution, it computed as the relative capacitor, and was 1.02. When the battery characteristic after 50 cycles was measured, and initial service capacity was made into 100%, the service capacity maintenance factor was 92.2%. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0035]It is a methyl 2-propynyl ape fight as example 7 alkyne derivative. [The inside of general formula (I), an $\text{R}^1=\text{R}^2=\text{R}^3$ = hydrogen atom, X= sulfoxide group, When Y= methyl group and n= 1] were used 2% of the weight to the electrolysis solution, and also the coin cell was produced like Example 6 and the battery characteristic was measured, the relative capacitor of initial service capacity was 1.02, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 91.8%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0036]It is a JI (1-methyl-2-propynyl) OGIZA rate as example 8 alkyne derivative. [The inside of general formula (I), an R^1 = hydrogen atom, an R^2 = methyl group, an R^3 = hydrogen atom, Used X= OGIZARIRU group, Y=1-methyl-2-propynyl group, and n= 1] 2% of the weight to the electrolysis solution, and also a coin cell is produced like Example 6, When the battery characteristic was measured, the relative capacitor of initial service capacity was 1.02, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 91.9%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0037]It is a methyl 2-propynyl OGIZA rate as example 9 alkyne derivative. [The inside of general formula (I), an $\text{R}^1=\text{R}^2=\text{R}^3$ = hydrogen atom, X= OGIZARIRU group, When Y= methyl group and n= 1] were used 2% of the weight to the electrolysis solution, and also the coin cell was produced like Example 6 and the battery characteristic was measured, the relative capacitor of initial service capacity was 1.03, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 91.1%. The low-temperature characteristic was also good. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0038]As example 10 positive active material, replace with LiCoO_2 and LiMn_2O_4 is used, Used the JI (2-propynyl) ape fight 2% of the weight as an alkyne derivative, and also prepare an electrolysis solution like

Example 6, and a coin cell is produced, When the battery characteristic was measured, the relative capacitor of initial service capacity was 0.83, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 93.1%. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0039]As example 11 positive active material, replace with LiCoO_2 and $\text{LiCo}_{0.2}\text{nickel}_{0.8}\text{O}_2$ is used, Used the JI (2-propynyl) ape fight 2% of the weight to the electrolysis solution as an alkyne derivative, and also prepare an electrolysis solution like Example 6, and a coin cell is produced, When the battery characteristic was measured, the relative capacitor of initial service capacity was 1.19, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 90.5%. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0040]As example 12 negative electrode active material, replace with an artificial graphite and natural graphite is used, Used the JI (2-propynyl) ape fight 2% of the weight to the electrolysis solution as an alkyne derivative, and also prepare an electrolysis solution like Example 6, and a coin cell is produced, When the battery characteristic was measured, the relative capacitor of initial service capacity was 1.02, and when the battery characteristic after 50 cycles was measured, the service capacity maintenance factor was 93.2%. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0041]The nonaqueous solvent of comparative example 2 PC/EC/DEC(capacity factor) =5/25/70 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF_6 at this. At this time, the alkyne derivative was not added at all. When the coin cell was produced like Example 6 using this electrolysis solution and the battery characteristic was measured, the service capacity maintenance factor was 81.8%. The manufacturing conditions and the battery characteristic of a coin cell are shown in Table 1.

[0042]

[Table 1]

	正極	負極	化合物	添加量 wt%	電解液組成 (容量比)	初期放 電容量 (相対 値)	50 サ イクル 放電容 量維持 率%
実施例 1	LiCoO ₂	人造 黒鉛	ジ(2-プロピニル)サル ファイト	0.5	1M LiPF ₆ PC/DMC=3/7	0.98	90.1
実施例 2	LiCoO ₂	人造 黒鉛	ジ(2-プロピニル)サル ファイト	2	1M LiPF ₆ PC/DMC=3/7	0.97	90.7
実施例 3	LiCoO ₂	人造 黒鉛	ジ(2-プロピニル)サル ファイト	5	1M LiPF ₆ PC/DMC=3/7	0.96	90.5
実施例 4	LiCoO ₂	人造 黒鉛	メチル 2-プロピニル サルファイト	2	1M LiPF ₆ PC/DMC=3/7	0.97	89.8
実施例 5	LiCoO ₂	人造 黒鉛	ジ(2-プロピニル)オギ ザレート	2	1M LiPF ₆ PC/DMC=3/7	0.97	90.2
比較例 1	LiCoO ₂	人造 黒鉛	なし	0	1M LiPF ₆ PC/DMC=3/7	0	充放電 しない
実施例 6	LiCoO ₂	人造 黒鉛	ジ(1-メチル 2-プロピ ニル)サルファイト	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.02	92.2
実施例 7	LiCoO ₂	人造 黒鉛	メチル 2-プロピニル サルファイト	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.02	91.8
実施例 8	LiCoO ₂	人造 黒鉛	ジ(1-メチル 2-プロピ ニル)オギザレート	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.02	91.9
実施例 9	LiCoO ₂	人造 黒鉛	メチル 2-プロピニル オギザレート	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.03	91.1
実施例 10	LiMn ₂ O ₄	人造 黒鉛	ジ(2-プロピニル)サル ファイト	2	1M LiPF ₆ PC/EC/DEC=5/25/70	0.83	93.1
実施例 11	LiCo _{0.2} Ni _{0.8} O ₂	人造 黒鉛	ジ(2-プロピニル)サル ファイト	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.19	90.5
実施例 12	LiCoO ₂	天然 黒鉛	ジ(2-プロピニル)サル ファイト	2	1M LiPF ₆ PC/EC/DEC=5/25/70	1.02	93.2
比較例 2	LiCoO ₂	人造 黒鉛	なし	0	1M LiPF ₆ PC/EC/DEC=5/25/70	1	81.8

[0043] This invention is not limited to the example of a statement, but various combination which can be guessed is easily possible for it from the meaning of an invention. The combination in particular of the solvent of the above-mentioned example is not limited. Although the above-mentioned example is related with a coin cell, this invention is applied also to a cylindrical shape and the cell of a square pillar form.

[0044]

[Effect of the Invention] According to this invention, the lithium secondary battery excellent in battery characteristics, such as a cycle characteristic in a wide temperature requirement, electric capacity, a conservation characteristic, can be provided.

[Translation done.]